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Two fiber-reinforced polymer composites were examined for susceptibility to microbiologically influenced degradation. Composites, resins, and fibers were exposed to sulfur/iron-oxidizing, calcareous-depositing, ammonium-producing, hydrogen-producing, and sulfate-reducing bacteria (SRB) in batch culture. Surfaces were uniformly colonized by all physiological types of bacteria. Epoxy and vinyl ester neat resins, carbon fibers, and epoxy composites were not adversely affected by microbiological species. SRB degraded the organic surfactant on glass fibers and preferentially colonized fiber-vinyl ester interfaces. Hydrogen-producing bacteria appeared to disrupt bonding between fibers and vinyl ester resin and to penetrate the resin at the interface.

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**MICROBIOLOGICALLY INFLUENCED DEGRADATION
OF FIBER REINFORCED POLYMERIC COMPOSITES**

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ABSTRACT

Two fiber reinforced polymer composites were examined for susceptibility to microbiologically influenced degradation. Composites, resins, and fibers were exposed to sulfur/iron-oxidizing, calcareous-depositing, ammonium-producing, hydrogen-producing and sulfate-reducing bacteria (SRB) in batch culture. Surfaces were uniformly colonized by all physiological types of bacteria. Epoxy and vinyl ester neat resins, carbon fibers, and epoxy composites were not adversely affected by microbial species. SRB degraded the organic surfactant on glass fibers and preferentially colonized fiber-vinyl ester interfaces. Hydrogen-producing bacteria appeared to disrupt bonding between fibers and vinyl ester resin and to penetrate the resin at the interface.

Keywords: polymer, composite, microorganism, degradation

INTRODUCTION

Fiberglass/polymer and carbon/polymer composite materials are used in many aquatic environments. With high strength to weight ratios and improved stiffness for high performance, these materials surpass conventional metals and alloys for many structural applications. Unfortunately, little attention has been paid to environmental degradation. It was long believed, for example, that fiberglass boat hulls would not suffer the corrosion, biofouling or deterioration found in conventional materials. However, it is now recognized that all engineering materials become colonized by microorganisms, including bacteria, within hours after exposure in natural waters.¹ Microorganisms grow and produce a viscoelastic layer or biofilm. The environment at the biofilm/material interface is radically different from the bulk medium in terms of pH, dissolved oxygen, and organic and inorganic species.² Furthermore, polymeric composites are subject to degradation from moisture intrusion and osmotic blistering.³ Although the problems of moisture intrusion and blistering have been studied⁴ and can be eliminated by proper manufacturing and maintenance procedures,⁵ repair costs and safety risks are high.

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Polymeric composites are subject to many kinds of environmental degradation. Tucker and Brown⁶ showed that carbon/polymer composites galvanically coupled to metals are degraded by cathodic reactions in seawater. Jones et al.⁷ demonstrated that epoxy and nylon coatings on steel were breached by mixed cultures of marine bacteria. Pendrys⁸ reported that p-55 graphite fibers were attacked by a mixed culture of *Pseudomonas aeruginosa* and *Acinetobacter calcoaceticus*, common soil isolates. Possible mechanisms for microbial degradation of polymeric composites include: direct attack of the resin by acids or enzymes, blistering due to gas evolution, enhanced cracking due to calcareous deposits and gas evolution, and polymer destabilization by concentrated chlorides and sulfides.

EXPERIMENTAL PROCEDURE

Identity and Maintenance of Bacterial Cultures

A sulfur/iron oxidizing bacterium, *Thiobacillus ferrooxidans*, Leathan strain, obtained from Dr. Norman Lazaroff, State University of New York, Binghamton, NY, was maintained in 9K medium⁹ containing 3.0 g (NH₄)₂SO₄, 0.1 g KCl; 0.5 g K₂HPO₄, 0.5 g MgSO₄·7H₂O, 0.01 g Ca(NO₃)₂ dissolved in 700 ml distilled water previously acidified to pH 2.5 with H₂SO₄. The salt solution was sterilized at 250°C and 150 psi for 15 minutes. Three hundred ml of an iron solution containing 44 g FeSO₄·7H₂O in pH 2.5 H₂SO₄ were filter sterilized and added to the salt solution.

Psuedomonas fluorescens, a calcareous-depositing bacterium, was obtained from the American Type Culture Collection (ATCC #17571), Rockville, MD. The organism was originally isolated from polluted seawater. *Ps. fluorescens* was maintained in a medium containing 0.25 g calcium acetate, 0.4 g yeast extract, 1.0 g glucose, 100 ml distilled water, and adjusted to pH 8.0 using NaOH.¹⁰

Lactococcus lactis subsp. *lactis*, ATCC #19435, an ammonium-producing bacterium, was maintained in brain heart infusion medium.¹¹ *Clostridium acetobutylicum*, ATCC #824, a bacterium previously shown to produce copious amounts of hydrogen from fermentation of sugars, was maintained in a growth medium described by Ford et al.¹² Sulfate-reducing bacteria (SKB), isolated as a mixed culture of facultative microorganisms from a corrosion failure of a carbon steel waster piece on a surface ship,^{13,14} were maintained in Postgate B growth medium.¹⁵

Exposure Conditions

Triplicate coupons (2.5 × 2.5 × 0.6 cm) of two fiber reinforced polymer composites—a carbon fiber (T-300) reinforced epoxy (NARMCO-5208/T-300, BASF)⁽¹⁾ (Figure 1a) and a glass (S-2) and carbon (T-300) reinforced vinyl ester (Derakane 411-45)⁽²⁾ (Figure 1b) were exposed to microbiological cultures for 161 days. The epoxy was cured in a vacuum bag autoclaved at 250°F. Vinyl ester resins were post-cured at 100°C for 8 hours. Additionally, carbon fibers, glass fibers, vinyl ester, and epoxy resins were individually exposed for 90 days to SRB and hydrogen-producing bacteria. Glass fibers had been treated with organofunctional Silane A-172⁽³⁾, a vinyl tris (2-methoxyethoxy) silane. All cultures were maintained at room temperature and were periodically refreshed with new media. Triplicate uninoculated controls were maintained under the same exposure conditions.

Moisture Uptake

Samples were weighed before and after exposure. Moisture uptake was calculated after the biofilm had been removed with a cotton swab containing acetone and the sample reweighed.

(1)Structural Materials, Anaheim, CA

(2)Dow Chemical, Midland, MI

(3)®Union Carbide, Danbury, CT

Surface Analysis

Samples were examined before and after exposure using an environmental scanning electron microscope (Electroscan Corporation, Wilmington, MA) coupled with an energy-dispersive x-ray analysis system (NORAN, Middleton, WI) (ESEM/EDS). The ESEM uses a secondary electron detector capable of forming high resolution images at pressures in the range of 0.1 to 20 torr. At these pressures, specimen charging is dissipated into the gaseous environment of the specimen chamber, enabling direct observation of uncoated, nonconductive specimens, including polymeric composites. If water vapor is used as the specimen environment, wet samples can be observed. Wet biofilms can be imaged directly without fixation, dehydration or metal coating, and EDS data can be collected at the same time sample morphology/topography is photographed.^{16,17} Exposed coupon samples were fixed in 2% glutaraldehyde, rinsed to distilled water, examined wet for evidence of degradation resulting from microbial activity, and compared to uninoculated controls.

RESULTS AND DISCUSSION

In all cases, composite, neat resin and fiber surfaces were colonized by all microbial types. Neither the epoxy nor the vinyl ester composites were adversely affected by calcareous-depositing or ammonium-producing bacteria. There was no evidence of attack of resins and fibers remained embedded within both resins. Composites exposed to sulfur/iron-oxidizing bacteria (Figure 2) were covered with crystalline deposits containing iron and sulfur in addition to microbial cells. All surfaces exposed to SRB were black due to the deposition of iron sulfides. No damage to the epoxy composite, epoxy neat resin, carbon fibers or vinyl ester neat resin could be attributed to the presence and activities of SRB and hydrogen-producing bacteria.

SRB grew preferentially at fiber/resin interfaces on the vinyl ester composite (Figure 3). Figure 4 shows unexposed glass fibers (Figure 4a), glass fibers exposed to uninoculated medium (Figure 4b), and glass fibers exposed to SRB in culture medium (Figure 4c). Glass fibers exposed to SRB lost all rigidity after the 90-day exposure so that the weave pattern was no longer evident. Control glass fibers remained rigid and maintained the original weave pattern. Glass fibers are routinely treated with an organic surfactant used to size the fibers and to facilitate handling. The silane surfactant promotes adhesion between the vinyl ester resin and glass fibers. Microbial degradation of the surfactant by SRB was further demonstrated with ESEM/EDS dot maps of silicon distribution (Figure 5). Dot maps of control fibers exposed to uninoculated media showed concentrations of silicon within the core of each fiber and small amounts of silicon along the length of each fiber. Similar maps for fibers exposed to SRB showed increased amounts of silicon along the length of the fiber. Many microorganisms are known to degrade organic polymers.^{18,19} The mixed anaerobic culture containing SRB used in this work has been shown previously to degrade marine caulks and traditional polymeric coatings.^{7,13,14}

Hydrogen-producing bacteria appeared to disrupt bonding between fibers and vinyl ester resin (Figure 6). The organisms penetrated the resin and disruption of fibers and resin may be due to gas formation within the composite.

Previous work published for moisture uptake for vinyl ester neat resin and the carbon vinyl ester composite indicate that the materials should be saturated after 90 days.²⁰ The neat resin and the carbon vinyl ester composite are typically saturated at 0.78 and 2.25% weight gain, respectively. In the presence of biofilms, moisture uptake was typically 0.1 and 0.9% for the neat resin and composite, respectively. It appears that biofilms may act as a diffusion barrier for water, retarding moisture uptake.

CONCLUSIONS

Epoxy resin and carbon fibers, either individually or in composite, were not degraded by sulfur/iron-oxidizing, hydrogen-producing, calcareous-depositing, or SRB. Bacteria did colonize resins, fibers and composites, but did not cause damage. SRB preferentially colonized vinyl ester composites at the fiber-resin interfaces. SRB did not degrade neat vinyl ester resin. SRB degradation of the organic surfactant on glass fibers was demonstrated with ESEM/EDS. Hydrogen-producing bacteria appear to have disrupted the fiber-vinyl ester resin bonding with penetration of the resin.

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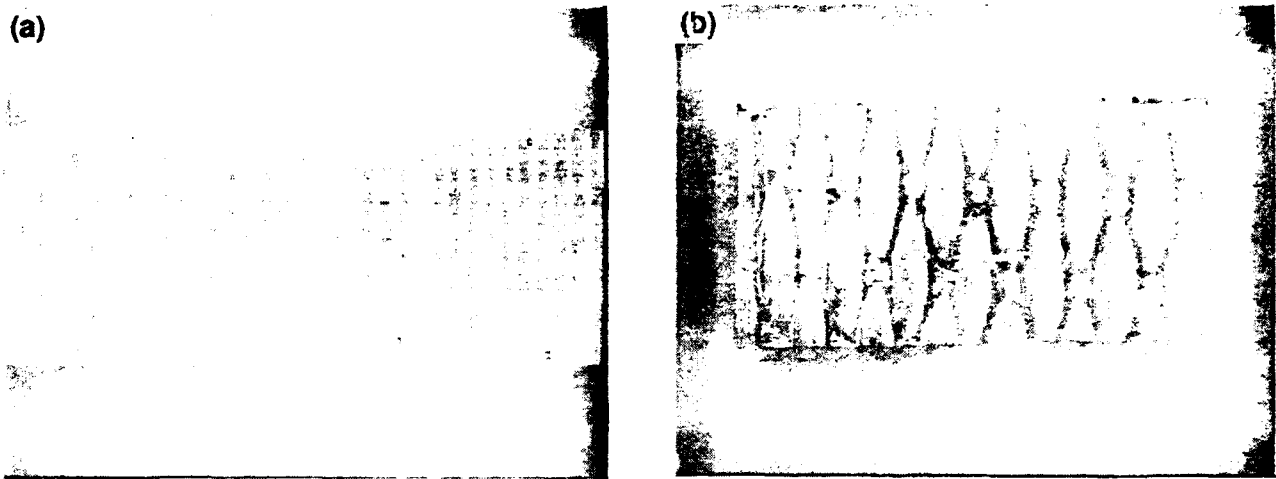


FIGURE 1 — Fiber reinforced polymer composite coupons (3×) (a) carbon fiber reinforced epoxy and (b) glass and carbon reinforced vinyl ester.

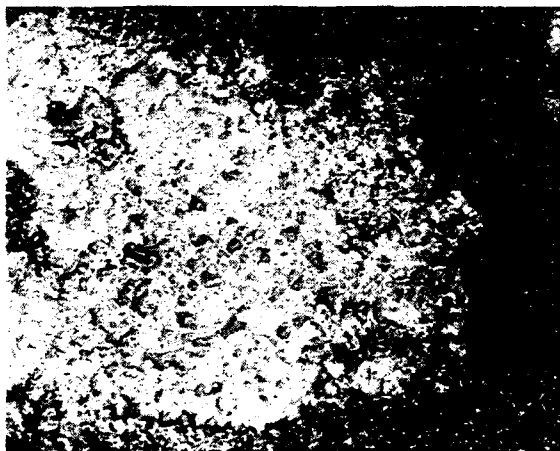


FIGURE 2 — Sulfur/iron-oxidizing bacteria with crystalline deposits on surface of fiber reinforced polymeric composite (3×).

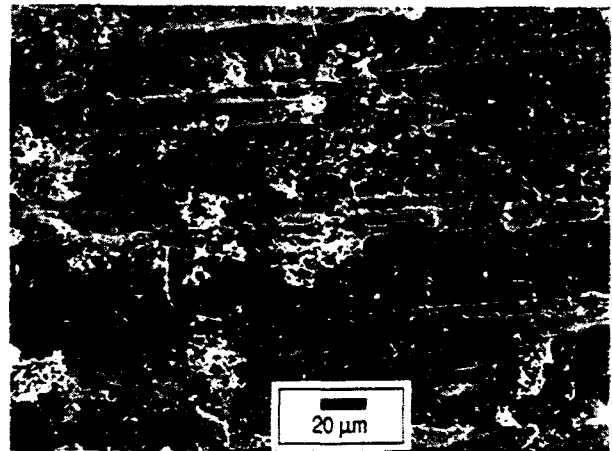


FIGURE 3 — SRB at fiber/resin interfaces of vinyl ester composite.



FIGURE 4 — Light microscope micrographs of glass fibers (2 \times) (a) unexposed, (b) exposed to culture medium, and (c) exposed to SRB in culture medium.

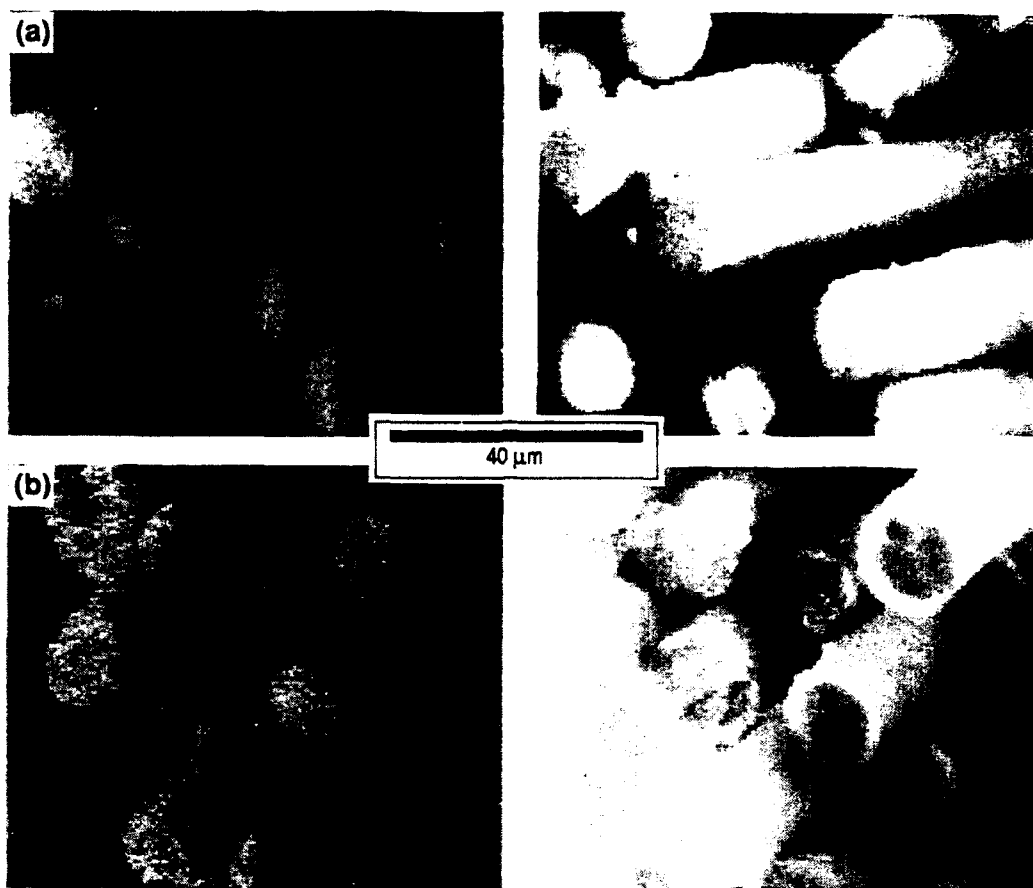


FIGURE 5 — EDS dot map of silicon for glass fibers (a) exposed to culture medium and (b) exposed to SRB in culture medium.

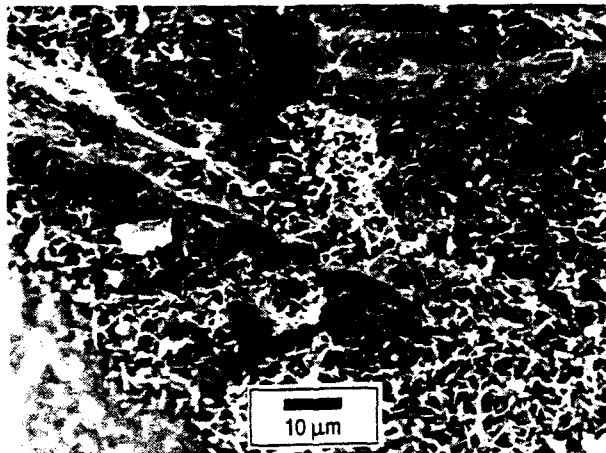
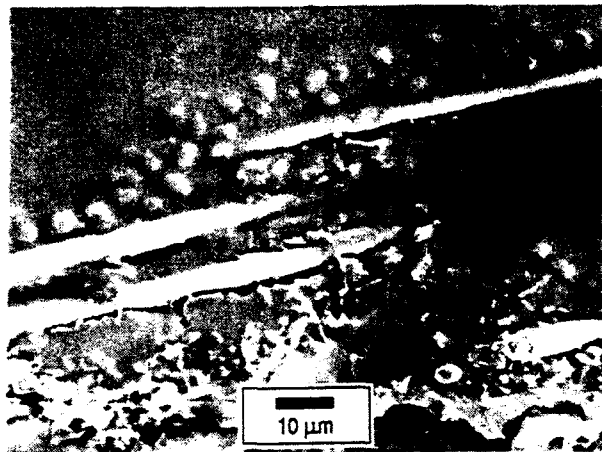
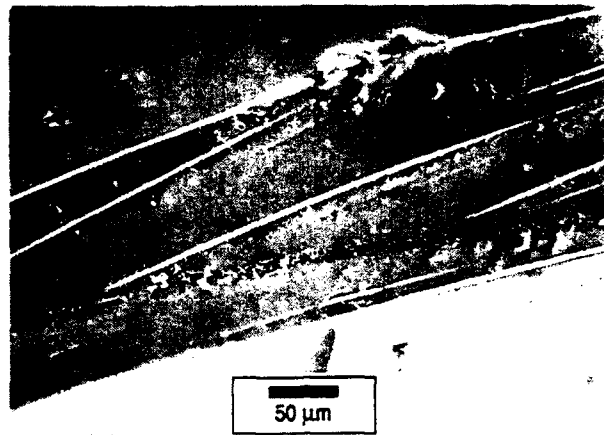


FIGURE 6 — Hydrogen-producing bacteria at disrupted interfaces between fibers and vinyl ester resin.